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Sulfur isotopic signals in two shallow ice cores from Dronning Maud Land, Antarctica

By ULF JONSELL[1]*, MARGARETA E. HANSSON[1], CARL-MAGNUS MÖRTH[2] and PETER TORSSANDER[2], [1]*Department of Physical Geography and Quaternary Geology, Stockholm University, 106 91 Stockholm, Sweden;* [2]*Department of Geology and Geochemistry, Stockholm University, Sweden*

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ABSTRACT

Sulfate deposited onto the Antarctic ice sheet originates from a mixture of sulfur sources. Two 100 m long ice cores from Dronning Maud Land have been studied by means of sulfur isotopic analysis and detailed ion analysis to reveal temporal and spatial differences in the influencing sulfur source. The two ice cores represent the coastal area and the polar plateau, respectively. The isotopic signals were similar within each ice core, indicating no temporal change of influencing sources during the last 1100 yr. The mean values at the two different sites were also similar: 14.6 ± 0.3‰ and 14.7 ± 0.3‰, respectively.

The similarity remains between calculated non-sea-salt values when a sulfate-depleted sea-salt aerosol is assumed in the costal core. When the influence of sporadic explosive volcanic eruptions is subtracted from the signal, the isotopic value from the polar plateau (15.4 ± 0.6‰) is significantly lower than prescribed values for marine biogenic sulfur. This suggests that one or more additional sources contribute to the sulfate budget. Several possible contributors are discussed in the context of former sulfur isotopic signals presented from Antarctica.

1. Introduction

Sulfate aerosols play an important role in the climate system by scattering the incoming solar radiation and by acting as cloud condensation nuclei. The current global climate forcing effect of sulfate aerosols is rather uncertain, but is estimated to be of the same order of magnitude as the effect of the anthropogenic component of greenhouse gases but opposite in sign (IPCC, 2001). Sulfate is the oxidized end product of different sulfur compounds in the atmosphere. Major natural sulfur sources are volcanic eruptions, marine and terrestrial biogenic activity, terrestrial windblown dust and sea salt. Marine biogenic production is estimated to be the dominant natural source in the Southern Hemisphere, while in the Northern Hemisphere the natural sulfur budget is dominated by inputs from volcanic activity (explosive eruptions and continuously degassing volcanoes), terrestrial dust and marine biogenic emissions (Legrand, 1995; Legrand et al., 1997). The globally dominating sulfur source today is anthropogenically induced emissions (Georgii and Warneck, 1999).

Polar ice sheets are useful climate archives. Analysis of ice cores drilled through the ice sheets reveals information about climate and atmospheric composition far into the past (e.g. EPICA Community Members, 2004). Sulfur in the ice is predominantly present as sulfate and to a minor extent as methanesulfonate (MSA). To understand variations in sources contributing sulfur to the ice sheet during glacial cycles a method is needed to distinguish between sulfates of different origin. The contribution from sea salt is commonly determined using the ratio of sulfate to another ionic species in sea water. MSA is an oxidized product of the dimethylsulfide produced by phytoplankton and has been used as proxy for the marine biogenic contribution to sulfate deposition (e.g. Legrand et al., 1991). However, it has been shown that MSA is altered by post-depositional processes (Wagnon et al., 1999; Pasteur and Mulvaney, 2000; Curran et al., 2002) and its validity as a tracer for biogenic sulfate is not as clear as previously thought (Delmas et al., 2003).

Sulfate originating from terrestrial sources can be linked to the dust flux, measured in ice cores by applying an average fraction of soluble sulfate in the lithospheric source material. The dust signal is often replaced with the Ca^{2+} record, which in general reflects the dust signal well, though the ratio of Ca^{2+} over dust is not stable over different climatic stages (Steffensen, 1997). Moreover, high calcium to dust ratios are found coinciding with volcanic sulfate peaks, when the sulfate probably originates from volcanoes as sulphuric acid rather than as lithospheric calcium carbonate or gypsum (Ruth et al., 2002), suggesting that the volcanic activity may distort a dust–calcium–sulfate relation.

A complementary method in apportionment of the sulfate source is the $^{34}S/^{32}S$ sulfur isotopic ratio. This method has been

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*Corresponding author.
e-mail: ulfj@natgeo.su.se

used since the 1950s (for an early review see Nielsen, 1974) and has recently been applied in various fields (e.g. Mast et al., 2001; Turekian et al., 2001; Peterson et al., 2003). In Polar snow and ice the use of sulfur isotopes has only recently been employed, and the number of studies is still few. Patris et al. (2000a) used the method on snow samples from the South Pole and calculated the contribution and isotopic value of marine biogenic and volcanic sources. Biogenic sulfate was concluded to be the main contributor of sulfate. Later the same method was implemented on Greenland ice core samples (Patris et al., 2002), where the industrial sulfur signal was also examined. Pruett et al. (2005) suggested, on the basis of West Antarctic sulfur isotopic data, a significant influx of stratospheric sulfate. Sulfur isotopic studies of the palaeoatmosphere were performed on samples from East Antarctic ice cores (Alexander et al., 2003) covering the last glacial period. The variation in sulfur isotopic values was attributed to a fractionation process during transport and no interpretation of the data from the perspective of source apportionment was presented.

We present the first comparison of sulfur isotopic data from two shallow ice cores representing different conditions in Dronning Maud Land, Antarctica: one is from the coastal area and one from the polar plateau. The isotopic and chemical data are used to assess the relative contribution from different sulfur sources with the aim of investigating spatial differences in contributing sources. The sulfur isotopic signals and the possible source contribution are discussed in the context of preceding sulfur isotopic measurements performed in Antarctica and elsewhere. The present limited knowledge of the spatial and temporal distributions of sulfur isotopic signals and contributing sulfur sources in Antarctica leads to apparent contradictory interpretations. We discuss the likelihood of other contributors, in addition to the evident ones of sea salt, marine biogenic and volcanic sources, to our samples, including degassing volcanoes, terrestrial dust and stratospheric sulphate. Moreover, we address shortcomings, such as the lack of confined isotopic ranges for the individual sources and limited knowledge about the fractionation of sulfur during atmospheric transport, in our discussion on the sulfur signals in Antarctic firn and ice.

2. Site description

Three 100 m long ice cores were drilled in Dronning Maud Land, Antarctica (Fig. 1) during an EPICA pre-site survey in 1997–1998 (Holmlund et al., 2000). One ice core was retrieved at Camp Victoria (core CV) (76°00′S, 08°03′W), which is located 550 km from the coast at 2400 m above sea level (a.s.l.) on the polar plateau, approximately 200 km south of the Heimefrontsfjella mountain ridge. The other two were drilled only 5 m apart at Camp Maudheimsvidda (CM, cores CMa and CMb) (73°06′S, 13°09′W) at 360 m a.s.l. CM is situated 140 km from the coast in the Vestfjella mountain range with several nunataks within tens of kilometres. The mean annual accumulation rate at core site CV is 61 mm water equivalence (mm w. eq.)

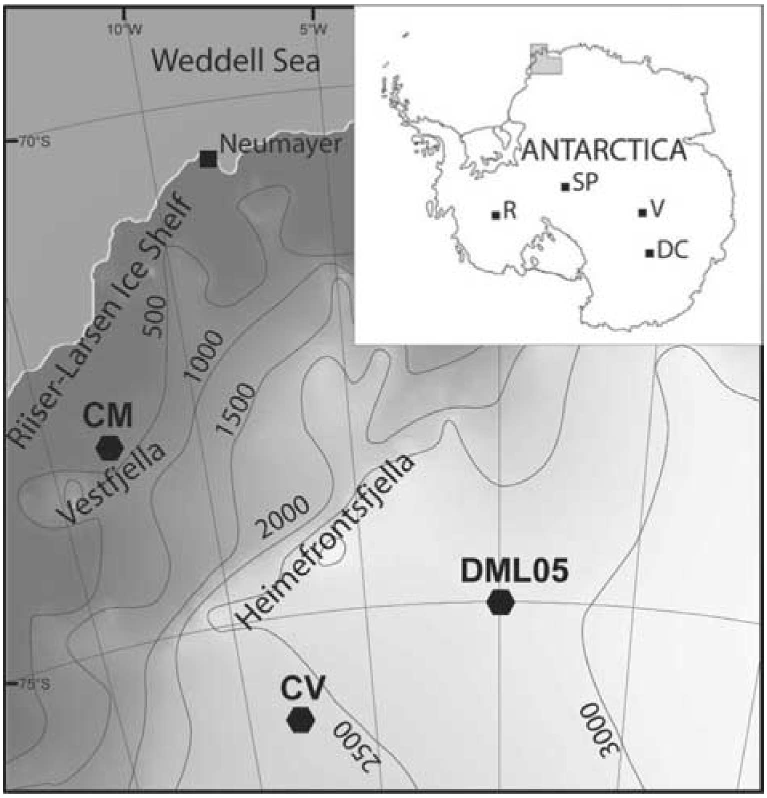

Fig. 1. Location of the core sites CM, CV and DML05 and of the other sites from where sulfur isotope data have been reported: SP, South Pole (Patris et al., 2000a); DC, Dome C and V, Vostok (Alexander et al., 2003); R, RIDSA (Pruett et al., 2005). Digital elevation data (Bamber and Bindschadler, 1997) were provided by the National Snow and Ice Data Center DAAC, University of Colorado, Boulder, CO.

Table 1. Sulfur isotopic composition and ion concentrations (in ppb), depth and approximate age range for the ice and firn samples from the CMa, CMb and CV cores

Sample	Depth (m)	Age[a] (yr)	$\delta^{34}S_{tot}$ (‰)	SO_4^{2-} mean (median)	Na^+	Mg^{2+}	MSA	Cl^-
CMa1	15.02–54.65	30–100	14.5±0.2	97	242	30	11	331
CMa2	55.00–84.69	100–200	14.8±0.2	93	170	18	12	300
CMa3	84.89–105.45	200–300	14.6±0.2	95	201	24	11	315
CMb_discrete[b]	50.30–57.85 ($n = 151$)			122 (94)	179	13	16	340
CV1	4.19–19.20	30–100	14.9±0.2	60	27	4	4	53
CV2	31.00–50.09	200–500	14.5±0.2	70	24	4	3	59
CV3	82.89–94.70	800–1100	15.0±0.2	67	18	3	6	42
CV_discrete[b]	19.20–31.00 ($n = 236$)			74 (62)	23	4	3	47
	50.15–56.75 ($n = 132$)			82 (67)	22	5	6	47
	62.05–75.85 ($n = 276$)			86 (72)	26	4	7	54
	94.70–119.60 ($n = 498$)			81 (74)	22	4	5	45

[a] Based on accumulation rates and volcanic horizons from Holmlund et al. (2000) and Karlöf et al. (2000).

[b] Mean value of all 5 cm samples within each section.

(Karlöf et al., 2000) and at CM it is 220 mm w. eq. (Holmlund et al., 2000).

3. Analyses

Six samples were analysed for sulfur isotopic composition. Three samples cover all of core CMa (Table 1) and three samples cover large sections of the CV core. The large sample sizes guarantee a time-integrated isotopic signal not disturbed by sporadic sulfate peaks and provide sufficient material for repeated isotopic analyses. Discrete samples on 5 cm resolution were retrieved in sections from the CMb core and from the remaining sections of the CV core.

Ice core samples were carefully decontaminated by removing the outer 0.5 cm of ice with a microtome on a laminar flow bench using clean-room clothing. The samples for isotopic analysis were thereafter melted and collected in thoroughly cleaned plastic drums and the laboratory work was performed in clean-room facilities. The initial sample volume was 65–110 l for each CMa sample and 10–30 l for each CV sample. Only the CMa samples were centrifuged at 30 000 rpm to extract all particles (for a study of the origin of the particles which will be reported elsewhere) before the isotopic analyses were performed. Repeated isotopic analyses, except for sample CV3, were performed five times for CMa samples and twice for CV samples. Aliquots of these samples were subjected to ion chromatographic analysis. The discrete 5 cm samples were similarly decontaminated and stored in frozen state in clean Accuvettes®. They were melted just prior to the ion chromatographic analysis.

The isotope samples were collected on an ion exchange column (strong basic anion resin, Sigma-Aldrich, no 21.740-9, Dionex 1 × 8–50, 20–50 mesh). The collected sulfate was eluted with 0.5 M NaCl and precipitated with 0.5 M $BaCl_2$ boiled for 1 min and adjusting the pH to about 2 with HCl. The $BaSO_4$ precipitate was left in a water bath for 2 h at about 90 °C. Thereafter the solution was cooled to room temperature and filtered through a polycarbonate filter (Millipore, Isopore, no HTTP 02500 or HTTP 04700, depending on the amount of $BaSO_4$ precipitated). The $BaSO_4$ collected on the filters was washed with ultraclean water (Elga Maxima Analytica) to remove Cl^- from the eluent and dried in an oven at 60 °C overnight. Filters were weighed and then scraped to remove the $BaSO_4$. It should be stressed that only the soluble sulfate is measured with this method and that other soluble sulfur-bearing compounds, such as MSA, do not contribute to the isotopic value.

The sample and standard mass ratios were measured using isotope ratio gas mass spectrometry (IRMS) in a mass spectrometer (Finnigan, model Delta+). All sulfur isotope measurements were done on $SO_{2(g)}$ converted from $BaSO_4$ on-line in a Carlo Erba NC2500 continuous flow system (CF-IRMS). Based on standard measurements the precision was better than ±0.2‰. $\delta^{34}S$ values are reported in ‰ according to

$$\delta^{34}S(‰) = \left(\frac{R_{sample}}{R_{STD}} - 1\right) \times 1000 \qquad (1)$$

where R_{sample} refers to the mass ratio $^{34}S/^{32}S$ of the sample and R_{STD} refers to the mass ratio of $^{34}S/^{32}S$ in Cañon Diablo troilite.

Concentrations of SO_4^{2-}, $CH_3SO_3^-$ (MSA), Cl^-, Na^+ and Mg^+ in all samples were measured on a Dionex IC500 ion chromatography system. (CMa and CV aliquots—anions: KOH eluent gradient, ASRS-ultra 2 mm suppressor; cations: MSA eluent gradient, CSRS-ultra 2 mm suppressor. CMb and CV 5 cm discrete samples—anions: NaOH eluent gradient, ASRS-I 2 mm suppressor; cations—H_2SO_4 isocratic gradient, CSRS-I 2 mm suppressor.) The analytical error is estimated to be less than 5%.

4. Results

The sulfur isotopic values for the soluble SO_4^{2-} in the firn/ice samples show low variation between the individual samples (Table 1) and the weighted mean values for the CMa and CV cores are almost identical at 14.6 ± 0.3‰ and 14.7 ± 0.3‰, respectively. The large sample sizes smooth the influence from high-magnitude low-frequency sulfur sources, such as large explosive volcanic eruptions. The low internal variation within the two cores indicates that no significant change in source contribution took place during the time period covered by the ice cores (about 300 and 1100 yr, respectively). Thus, the anthropogenic emissions of sulfate during the last decades cannot be detected in the sulfur isotopic signal at these sites in Antarctica.

Na^+, Cl^-, SO_4^{2-} and Mg^{2+} concentrations of the aliquots and the mean values for the 5 cm discrete sample sections are presented in Table 1. The concentrations of both sea-salt species (Na^+, Cl^-, SO_4^{2-}, Mg^{2+}) and MSA are higher in the CM core samples than in the CV core samples. Sulfate concentrations are about 50% higher in the samples of the CMa core than in the CV core. The SO_4^{2-} concentrations of the aliquots within each core exhibit small variations: CMa 95–97 ppb and CV 60–70 ppb. The mean SO_4^{2-} concentrations of the discrete samples are slightly higher than the corresponding aliquots of the sulfur isotope sample. However, the 5 cm discrete samples were cut in selected sections where volcanic horizons were expected based on the ECM profiles presented in Holmlund et al. (2000) and could possibly explain the slightly higher mean sulfate concentrations. The median concentrations therefore correspond better to the mean values of the aliquots. The detailed chemistry of the two ice cores will be reported elsewhere.

5. Discussion

5.1. *Sulfate depletion and $\delta^{34}S_{nss}$*

The sulfur isotopic signal of the samples ($\delta^{34}S_{tot}$) is determined by the contributing fraction to total SO_4^{2-} concentration ($totSO_4^{2-}$) (f_{SX}) and isotopic value $\delta^{34}S_{SX}$ of each source as a weighted average:

$$\delta^{34}S_{tot} = \delta^{34}S_{S1} f_{S1} + \delta^{34}S_{S2} f_{S2} \cdots + \delta^{34}S_{Sn} f_{Sn} = \delta^{34}S_{ss} f_{ss} + \delta^{34}S_{nss} f_{nss}. \quad (2)$$

The subscript ss denotes sea-salt SO_4^{2-} and nss non-sea-salt SO_4^{2-} (i.e. all other sources). $\delta^{34}S_{nss}$ can be obtained by using simple algebra on eq. (2):

$$\delta^{34}S_{nss} = \left[\delta^{34}S_{tot} - (1 - f_{nss}) \times \delta^{34}S_{ss}\right] / f_{nss} \quad (3)$$

where $\delta^{34}S_{tot}$ is the measured isotopic value of the sample, $\delta^{34}S_{ss}$ is the sulfur isotopic signal of sea water (21‰, Rees et al., 1978) and f_{nss} the fraction of $nssSO_4^{2-}$ to $totSO_4^{2-}$.

The $nssSO_4^{2-}$ contribution is usually calculated by using the SO_4^{2-} to Na^+ ratio (k) in standard sea water via:

$$[nssSO_4^{2-}] = [totSO_4^{2-}] - ([Na^+] \times k). \quad (4)$$

However, k has been shown to break down for snow and ice deposited in coastal Antarctica (Minikin et al., 1994; Hall and Wolff, 1998; Wagenbach et al., 1998) because it generates preposterous negative $nssSO_4^{2-}$ concentrations which have been detected up to 300 km from the coast (Minikin et al., 1994). Rankin et al. (2000) suggested this depletion process to be due to the precipitation of mirabilite ($Na_2SO_4 \cdot 10H_2O$) which forms during frost flower formation on the Antarctic sea ice. Neither the process nor the spatial extent of the depletion of sulfate with respect to sodium is fully understood, but seems to be infrequent at altitudes as high as the Antarctic plateau (Aristarain and Delmas, 2002), which encompasses the location of core site CV. However, there has been a recent suggestion that a sulfur-depleted aerosol scoured from the sea ice surface is the dominant source of sea-salt aerosol to central Antarctica as well (Wolff et al., 2003). But no chemical record supporting this suggestion has yet been presented.

In order to detect if sulfate depletion is present on core sites CM and CV, respectively, $nssSO_4^{2-}$ was first calculated using the standard sea water ratio ($k = 0.25$). The calculation produces several negative $nssSO_4^{2-}$concentration values on CMa and a weak relation between Na^+ and $nssSO_4^{2-}$ (Fig. 2). On CV, neither negative concentrations nor any relation with Na^+ is seen. The result on the CMa samples indicates that the calculation overestimates the sea-salt SO_4^{2-} fraction and that a depletion of sulfate is present. To further estimate the size of the depletion on CM, the value of k corresponding to the minimal correlation between Na^+ and $nssSO_4^{2-}$ was sought, which could be a reasonable assumption for two species of different origin. In order to assess the sensitivity of the method, the calculation was made by randomly selecting 75% of the data separately for 1000 calculations. The mean value and standard deviation of the obtained k was 0.09 ± 0.02, which covers $k = 0.07$ as found for sulfate depleted aerosols in coastal Antarctica by Wagenbach et al. (1998), a figure subsequently used by others (Legrand and Pasteur, 1998; Minikin et al., 1998; Kerminen et al., 2000). A similar analysis for detecting the sulfate depletion in several firn cores from the Filchner–Ronne Ice Shelf yielded somewhat lower k values (0.043–0.058) (Minikin et al., 1994), but considered, in contrast to this work, only samples from the winter season when the depletion process is likely to be more effective

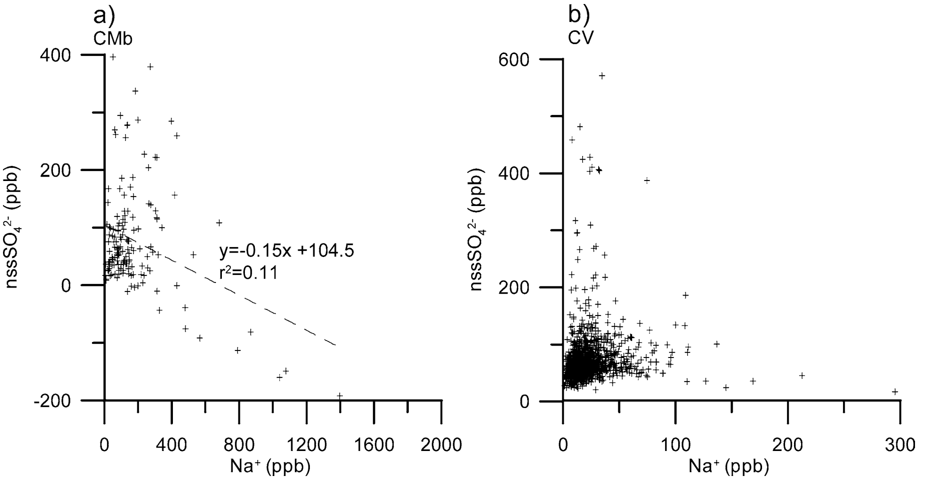

Fig. 2. Scatter plot of Na^+ and SO_4^{2-} of the 5 cm discrete samples for (a) core CMb ($n = 151$) and (b) CV ($n = 1140$), respectively. Note the different scales.

Table 2. $\delta^{34}S_{tot}$, $\delta^{34}S_{nss}$ and nssSO_4^{2-} concentration calculated assuming sea water ratio ($k = 0.25$) or a sulfate depletion ratio ($k = 0.09 \pm 0.02$). Bold figures indicate the assumed state and are used for subsequent calculations (see text)

Sample	$\delta^{34}S_{tot}$ (‰)	$\delta^{34}S_{nss}$ (‰)		nssSO_4^{2-} (ppb) (% of totSO_4^{2-})	
		$k = 0.25$ (sea water ratio)	$k = 0.09 \pm 0.02$ (depletion ratio)	$k = 0.25$ (sea water ratio)	$k = 0.09 \pm 0.02$ (depletion ratio)
CMa1	14.5±0.2	4.5 ± 2.7	**12.7 ± 0.8**	39 (36%)	**76** (79%)
CMa2	14.8±0.2	9.5 ± 1.3	**13.5 ± 0.6**	51 (55%)	**78** (84%)
CMa3	14.6±0.2	7.2 ± 1.8	**13.1 ± 0.7**	49 (52%)	**77** (81%)
CV1	14.9±0.2	**14.1 ± 0.4**	14.6 ± 0.4	**53** (89%)	57 (96%)
CV2	14.5±0.2	**13.9 ± 0.4**	14.3 ± 0.4	**64** (91%)	68 (97%)
CV3	15.0±0.2	**14.5 ± 0.4**	14.8 ± 0.4	**62** (93%)	65 (98%)

(Wagenbach et al., 1998). The non-existence of negative nssSO_4^{2-} concentrations on the CV samples does not allow us to rule out that sulfate depletion occurs at this site, but the contribution of sea-salt SO_4^{2-} with $k = 0.25$ is limited to 7–11% (Table 2) and alters the nssSO_4^{2-} concentrations by only 3–4 ppb.

Based on our findings, and in conjunction with the reported studies on sulfate depletion, we suggest that the nss SO_4^{2-} concentrations from core site CM must be calculated considering a SO_4^{2-} depletion. The appropriate value of k is difficult to assign, but our obtained value of $k = 0.09 \pm 0.02$ is used in the subsequent calculations. $\delta^{34}S_{nss}$ are presented for both a depleted and non-depleted aerosol in order to compare the impact on the isotopic value (Table 2). Calculation of $\delta^{34}S_{nss}$ was performed by a Monte Carlo simulation (2000 runs) with the error limits stated for each parameter included in eqs (3) and (4) treated as standard deviation on a normal distribution and with the mean determined by the measured or known value. On the CMb samples the difference in isotopic value is large depending on the calculation method used and error limits increases with f_{ss}. On the CV samples the changes in isotopic values are within the error limits. In the following discussion the $\delta^{34}S_{nss}$ values calculated considering SO_4^{2-} depletion on CM and with the standard sea water ratio on CV, respectively, are used.

5.2. *Contributors to nssSO_4^{2-}*

The almost identical $\delta^{34}S_{tot}$ values from the sites CMa and CV (Table 2) remain after subtraction of the sea-salt contribution. The $\delta^{34}S_{nss}$ values are slightly lower in CMa (12.7–13.5‰) than in the CV core (13.9–14.5‰), but considering the error limits they are indistinguishable. Thus, the isotopic signal gives no straightforward evidence for a difference in nssSO_4^{2-} contribution.

The difference in MSA concentration cannot can be used either as evidence for different sulfur sources for the sites, since the lower MSA concentration in the CV samples is probably an effect of a post-depositional loss. Wagnon et al. (1999) found that the loss of MSA is particularly pronounced at sites where the annual mean accumulation rate is less than 60 mm w. eq. and very limited on sites where mean accumulation is higher than higher than 200 mm w. eq. These limits correspond well to the mean annual accumulation rate of CV and CM (61 and 220 mm w. eq., respectively). Since the isotope analysis is performed only on sulfur from soluble SO_4^{2-}, any post-depositional loss of MSA will not affect the isotopic values.

Sulfate inputs from sporadic explosive volcanic eruptions are detected as distinct peaks in SO_4^{2-} records from ice cores. The background sulfur isotopic signal originates from all contributors to $nssSO_4^{2-}$ except the explosive volcanic eruptions. Its isotopic value ($\delta^{34}S_{bg}$) can be calculated by subtracting the contribution from explosive volcanic eruptions from $nssSO_4^{2-}$ signal following the additive principle of eq. (2):

$$\delta^{34}S_{bg} = \left(\delta^{34}S_{nss} - f_{vol} \times \delta^{34}S_{vol}\right)/(1 - f_{vol}). \qquad (5)$$

This procedure requires that the relative contribution of volcanic sulfate to $nssSO_4^{2-}$ in the ice core sample (f_{vol}) and the isotopic signal of the volcanic SO_4^{2-} ($\delta^{34}S_{vol}$) are known. For core site CV these data have been obtained with the following methods and assumptions:

(1) Traufetter et al. (2004) detected and calculated the individual sulfate flux for all volcanic peaks in core DML05 from Dronning Maud Land, 250 km east of core site CV (Fig. 1). The relative SO_4^{2-} contribution from the volcanic peaks in DML05, calculated as the sum of all volcanic peaks divided by the total $nssSO_4^{2-}$ flux in DML05, yields 10 ± 3% (Table 3). Considering the relative proximity of the cores on the polar plateau along with similar accumulation rate and mean $nssSO_4^{2-}$ concentrations, this calculated relative load from explosive volcanoes is assumed to be representative of the CV core as well.

(2) Sulfates of volcanic origin have variable isotopic signals, depending on the source material for the volcano and type of emission to the atmosphere (ash or gas). The stratospheric input is most likely to originate from oxidized $SO_{2(g)}$. The signal of $\delta^{34}S_{vol}$ is for volcanic gas emissions confined between 0–5‰ (Nielsen et al., 1991) and is in agreement with findings from Antarctica (Patris et al., 2000a). Considering the great number of volcanoes (49) found in the DML05 core (Traufetter et al., 2004) this range is assumed to be representative for the integrated volcanic signal in the CV core

The deposition on the ice sheet of sulfate from explosive volcanic eruptions is temporally irregular and the three samples of the CV core are not expected to have the same relative contribution of volcanic SO_4^2. The discrete 5 cm SO_4^{2-} record of the CV core does not correspond to the length sections where the samples for sulfur isotopes were cut (Table 1). Consequently, separate volcanic eruptions, as detected in the DML05 core, cannot be attributed to the individual sulfur isotope sample of CV. The weighted mean $\delta^{34}S_{nss}$ of the three CV samples (14.1 ± 0.3‰) is therefore used as an average for the whole core. Considering the large sample sizes, covering almost half of the core length (Table 1), and the small variation in mean SO_4^{2-} concentration and $\delta^{34}S$ of the individual samples, this value is assumed to be representative.

A Monte Carlo simulation (2000 runs) on eq. (5) to obtain the integrated $\delta^{34}S_{bg}$ for CV, using $\delta^{34}S_{nss} = 14.1 \pm 0.3$‰ and f_{vol} 10% ± 3% as means and standard deviations on a normal distribution, respectively, and $\delta^{34}S_{vol}$ 0–5‰ on a uniform distribution, yields $\delta^{34}S_{bg} = 15.4 \pm 0.6$‰.

In Antarctica the background $nssSO_4^{2-}$ has been suggested to be of predominantly marine biogenic origin (Legrand, 1995). But the $\delta^{34}S_{bg}$ at core site CV is significantly lower than the value for a regionally integrated marine biogenic source ($\delta^{34}S_{mb} = 18.6 \pm 0.9$‰) in snow from the South Pole (Patris et al., 2000a). The South Pole samples represent a time period between about 1930–1970 and are thus not perfectly comparable with the samples presented here. On the other hand the small difference in $\delta^{34}S$ between the CV samples indicates stable isotopic conditions during the time period. Moreover, there is an analytical

Table 3. Comparison of age, accumulation, elevation and sulfate fluxes between cores DML05 and CV (n.a. = data not available)

	DML05	CV
Time period covered	A.D. 461–1997[a]	A.D. 540–1997[b]
Accumulation rate (mm w. eq.)	60[c]	61[b]
Elevation (m a.s.l.)	2900[a]	2400
Mean $nssSO_4^{2-}$ conc. (ppb)	64	62
Total $nssSO_4^{2-}$ flux (kg km^{-2})	6930 [d]	n.a.
Total explosive volcanic SO_4^{2-} flux (kg km^{-2})	670±220	n.a.
Explosive volcanic $SO_4^{2-}/nssSO_4^{2-}$(%)	10±3	n.a.

[a] Traufetter et al. (2004).
[b] Karlöf et al. (2000).
[c] Sommer et al. (2000).
[d] H. Fischer, personal communication 2003.

difference in that the South Pole samples also include the MSA signal, but this should only account for ± 0.5‰ (Patris et al., 2000a). Both the South Pole $\delta^{34}S_{mb}$ and the CV $\delta^{34}S_{bg}$ value fall within a theoretical range on $\delta^{34}S_{mb}$ (Calhoun et al., 1991), but several reports on $\delta^{34}S_{mb}$ suggest a value in the middle of this range, near 18‰ (Newman et al., 1991; Norman et al., 1999), in concordance with the small depletion in ^{34}S found in plankton (Nriagu et al., 1991). Measurements on marine aerosols from the southern Pacific Ocean (Calhoun et al., 1991) and the Atlantic Ocean (Patris et al., 2000b) yielded $\delta^{34}S_{nss}$ similar to or lower (minimum 12.5‰) than the $\delta^{34}S_{bg}$ for core site CV, but they were probably influenced by isotopically lighter continental sulfuric components (Patris et al., 2002). It cannot be ruled out that $\delta^{34}S_{bg}$ at core site CV is of entirely biogenic origin, lacking a precise value of $\delta^{34}S_{bg}$. In either case, the difference between $\delta^{34}S_{bg}$ at core site CV and the $\delta^{34}S_{mb}$ values found by Patris et al. (2000a) on the South Pole remains enigmatic and demands an explanation. We will now discuss the possibilities of additional significant sources—constantly degassing volcanoes, terrestrial dust and stratospheric background SO_4^{2-}.

The fluxes from constantly degassing volcanoes and/or smaller regional eruptions are not captured as peaks in the sulfate record of the DML05 core and are therefore not accounted for in eq. (4). SO_4^{2-} from constantly degassing volcanoes is considered a significant component of the sulfur budget on Greenland, due to its more proximate location to continental areas (Legrand, 1995). In contrast to explosive eruptions, the SO_4^{2-} flux from constantly degassing volcanoes does normally not reach the stratosphere. Thus, the flux could give regional imprints and is likely to be different between core site CV and the South Pole. The Antarctic region encompasses a number of volcanically active areas (Delmas et al., 1985; Basile et al., 2001) and 31 volcanoes are listed in the Smithsonian volcano database (http://www.volcano.si.edu/world/). Most probable sources for core site CV are the volcanic areas around the Antarctic Peninsula (South Shetland Island and James Ross Island), together with the southern Andes, following the storm tracks of the Southern Hemisphere. In order to obtain the $\delta^{34}S_{bg}$ at core site CV (15.4 ± 0.6‰), the required impact on the isotopic balance for this possible additional volcanic source must be about 2‰ assuming the remaining contributor to be of marine biogenic origin with $\delta^{34}S_{mb} \sim 18‰$. The relative SO_4^{2-} contribution of constantly degassing volcanoes and/or small volcanic eruptions to the sulfate budget at core site CV would then be about 10–20%, assuming similar values of $\delta^{34}S_{vol}$ for degassing and explosive volcanoes (0–5‰), following the principles of the isotopic balance equation (eq. 2).

Soluble terrestrial SO_4^{2-}-bearing dust can originate either from sources in the Antarctic region (snow-free coastal areas and nunataks) or by more long-range transport from source areas on the ice-free continents. The long-range transported dust deposited in glacial periods on Vostok and Dome C in East Antarctica is suggested from Sr/Nd data to originate from Patagonia (Delmonte et al., 2004; Basile et al., 1997), where CM and CV are along the transport trajectories. Crustal sulfur has a wide isotopic range with, on average, slightly positive values, but large variations exist depending on the location (Nielsen et al., 1991). If terrestrial dust was responsible for the difference between $\delta^{34}S_{bg}$ at core site CV (15.4 ± 0.6‰) and the estimated $\delta^{34}S_{mb} \sim 18‰$, the terrestrial dust must have a lighter $\delta^{34}S$ signal than $\delta^{34}S_{bg}$ at core site CV. Core site CM is nearer to nunataks than core site CV and the influence of local terrestrial dust would thus be expected to be higher than for core site CV. If the local source was significant on core site CM, the $\delta^{34}S_{nss}$ value for core site CM would be expected to be significantly different from that of core site CV. Moreover, the rock type of the nunataks in the vicinity of core site CM are not sulfate evaporites but basalts (Luttinen and Furnes 2000) and not expected to dissolve SO_4^{2-} in the melted ice and firn samples. If excluding the local dust source, the long-range transported dust still remains but is difficult to quantify. From other Antarctic sites the terrestrial sulfate has been calculated to account for a minor part (0–2% on Vostok Holocene samples, Alexander et al., 2003, and negligible on Neumayer, Minikin et al., 1998).

Background stratospheric SO_4^{2-} (in contrast to elevated SO_4^{2-} concentrations in the stratosphere due to recent volcanic eruptions) has been determined to have $\delta^{34}S$ values of 2.6 ± 0.3‰ (Castleman et al., 1973). A stratospheric background source had a significant impact in a sulfur isotopic study from West Antarctica (Pruett et al., 2005). The samples represented the period A.D. 1937–1974 and $\delta^{34}S_{nss}$ ranged from −0.7 to 6.8‰. This range is not consistent with a dominating marine biogenic source to the Antarctic SO_4^{2-} budget, and was explained by a major contribution from a light stratospheric source of about 50% of the total $nssSO_4^{2-}$. At the coastal station Neumayer (Fig. 1) the stratospheric SO_4^{2-} flux from intrusion of stratospheric air masses based on ^{10}Be measurements together with the gravitational settling of SO_4^{2-} formed in polar stratospheric clouds accounted for an absolute maximum in airborne SO_4^{2-} to 15% of $nssSO_4^{2-}$ during the winter season (Minikin et al., 1998)—a figure that is significantly smaller (below 5%) during the summer season. However, on a site at higher altitude and latitudes than core site CV or the West Antarctic site in Pruett et al. (2005) (1740 m a.sl.) the fraction of stratospheric input would be expected to be higher due to both the lower absolute $nssSO_4^{2-}$ concentration and a higher stratospheric influx. If so, we would expect the impact on the sulfur isotopic signal to show lower values at core site CV than for the lower-lying core site CM. In fact, the CV samples have slightly higher $\delta^{34}S_{nss}$ values (Table 2). On the basis of isotopic data from two East Antarctic sites (Dome C and Vostok), covering the last glacial cycle, a solution which apportioned the sources with approximately 50% non-biogenic sources (dust or stratospheric sulfate) was, as in Pruett et al. (2005), discussed but eventually ruled out based on the relation between O and S isotopes in SO_4^{2-} (Alexander et al., 2003). The results are not directly comparable due to both the different location and different temporal coverage, but the contradicting interpretations call for further assessment of the importance of the stratospheric flux in Antarctica.

An additional factor not relating to a specific source, and which may possibly affect the isotopic signal significantly, is fractionation of S during oxidation of SO_2 to SO_4^{2-}. Heterogeneous (gas–liquid) oxidation of SO_2 has been shown in laboratory experiments (Eriksen, 1972) and in *in situ* measurements (Newman et al., 1975) to enrich the oxidation product (SO_4^{2-}) in ^{34}S. Studies on homogeneous (gas–gas) oxidation have yielded opposite results (Tanaka et al., 1994; Leung et al., 2001). In the present conditions of the troposphere heterogeneous oxidation is believed to the account for the dominant part of oxidation globally (Jacob 2003) because of it being a faster reaction and the presence of liquid water suspended in the air. SO_2 has a residence time of a few days and the SO_2 from distant sources will therefore oxidize prior to arrival to the Antarctic continent, while SO_2 derived from DMS from the polar ocean will be oxidized in the atmosphere over the continent. However, the oxidation pattern may have been different during past climate conditions. Alexander et al. (2003) explained lower sulfur isotopic values during the last glacial period as due to an increased amount of homogeneous oxidation due to the drier climate, with a progressively isotopic lighter SO_2 content of the air propagating inwards the Antarctic continent and consequently an isotopically lighter oxidation product (SO_4^{2-}). If this fractionation process also is active during the present climate, we would expect lower $\delta^{34}S_{bg}$ on the central Antarctic sites compared with peripheral sites. The few sites and data from Antarctica give no confirmation of this theory: Samples including snow/firn from the twentieth century from the most central location (South Pole) have higher $\delta^{34}S_{bg}$ values (17.9‰, 17.5‰ in Patris et al., 2000a) than CM, CV and the West Antarctic samples (Pruett et al., 2005). Fractionation may therefore not be a first-order process for variance in the sulfur isotopic record in the present climate.

The above discussion on $\delta^{34}S_{bg}$ has been focused on core site CV due to its relative proximity to core site DML05. A similar relative SO_4^{2-} load from explosive volcanic activity at the core site CM must entail higher fluxes of volcanic sulfate due to the higher $nssSO_4^{2-}$ concentrations (Table 2). A difference in transport trajectories between the core sites CM and CV could alter the relative contribution from a regional source, but the distance between the sites is only 400 km. The similar $\delta^{34}S_{nss}$ values also suggest a similar source contribution with contribution to the sulfur budget at similar relative levels.

6. Conclusions

The sulfur isotopic signals from two ice cores from Dronning Maud Land exhibit temporal and spatial stability. The large sample sizes guarantee a time-integrated signal but prevent investigation of short-term variations. However, no influence of anthropogenic sulfate emissions in the last decades seems to have altered the signal. The $\delta^{34}S_{nss}$ values for the samples from core site CM are highly dependent on the sulfate to sodium ratio used in the calculation. The sea-salt aerosol seems to be depleted in SO_4^{2-} with respect to Na^+ at the coastal core site CM (i.e. possessing a smaller ratio compared with standard sea water). On the polar plateau core site CV, the sea-salt fraction is either too small to reveal a depletion or it is not depleted, possibly indicating an origin from lower—sea-ice-free—latitudes without active fractionation processes. However, in either case the standard sea water ratio can be used for the samples from the CV core. The calculations of the $nssSO_4^{2-}$ component for CV and CM with different ratios gives similar $\delta^{34}S_{nss}$ values for the two sites.

The relative load of explosive volcanic SO_4^{2-} at core site CV can be determined to 10 ± 3% by comparison with a closely located core (DML05). After subtracting this contribution, the remaining background sulfur isotopic signal in the CV samples suggests, due to the relatively low value, that the marine biogenic source may not be the only significant sulfur source in this area. The additional source cannot be identified, but one probable candidate is an additional input from constantly degassing volcanoes. A stratospheric background SO_4^{2-} contribution could also be significant but the expectation that the CV site, being located at higher latitude and altitude, would have a higher stratospheric flux contradicts the similar $\delta^{34}S_{nss}$ values found in the CM and CV samples. SO_4^{2-} from terrestrial dust cannot be definitively ruled out as a contributor, but is believed to have little impact.

An alternative explanation for the relatively low background sulfur isotopic value is that the marine biogenic source in reality is lower than the values reported elsewhere of around 18‰. If so, former results from this frequently quoted and utilized figure must be reconsidered. Increased knowledge about, and a better confined value of, the marine biogenic source would significantly improve all source apportionments of sulfur compounds in the atmosphere.

The extent of fractionation processes on the $\delta^{34}S$ signal is sparsely known, but the few data from Antarctica hitherto contradict fractionation during transport, with a progressively lighter $\delta^{34}S$ in SO_4^{2-}, as in the present climate, being a first-order factor of $\delta^{34}S$ variation in Antarctica.

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